# ELECTROCHEMICAL DESTRUCTION OF METHIDATHION BY ANODIC OXIDATION USING A BORON-DOPED DIAMOND ELECTRODE

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The degradation of insecticide methidathion (organophosphorous pesticide) in aqueous medium has been studied by anodic oxidation using a boron-doped diamond (BDD) anode. The results obtained show that the application of electrolysis of pesticide allows to reduce the chemical oxygen demand (COD). For 2 % NaCl and 3 % NaCl solutions the achieved reduction was 85 % and 72 % respectively. In all cases, the pH of electrolysis was significantly reduced after 45 min. The COD of methidathion solution was observed to fall with pseudo first-order kinetics. An increasing of applied current leads to an increase of the rate of electrochemical oxidation process. The effect of temperature shows that for 25 °C and 65 °C the achieved reduction was 85 % and 66 % respectively. The activation energy indicates that the process of electrochemical degradation is a complex one.

**Keywords:** ecology of water resources, electrochemical oxidation, pesticide, methidathion, ecology

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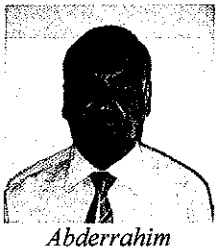

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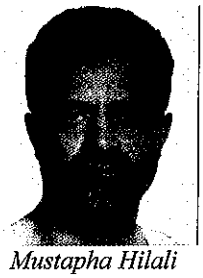

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## Introduction

The disposal of pesticides can cause serious problems due to the chemical nature of the active ingredients in pesticide formulation and due to the large quantities of the unwanted products. These products undergo physical and chemical alterations either due to extended storage, beyond the recommended expiry date, or storage under improper conditions (high humidity and temperature). In many countries, large quantities of pesticides have accumulated since they have lost their desirable characteristics. Pesticides that have passed their self-life

can be included in this category. Although, these products are not suitable for use, they still contain toxic compounds. In addition, many surplus pesticides, still within their expiration limits, may become useless, when their future use is prohibited due to toxicological or environmental concerns [1].

Recently, there has been increased interest in the use of electrochemical method for wastewater treatment. Electrochemical methods have been successfully applied to the purification of wastewaters containing phenolic substances [2], cyanides [3], refractory organic pollutants [4], olive oil production units [5], wastewaters generated in textilemanufacture [6] and tanneries [7].

The recent use of a boron-doped diamond (BDD) thin film anode [8-12] in anodic oxidation has shown that its $O_2$ overvoltage is much higher than that of conventional anodes such as $PbO_2$, doped $SnO_2$, $IrO_2$ and Pt, then producing larger amounts of adsorbed OH• by reaction

$$Cl_2 + H_2O \Leftrightarrow HClO + H^+ + Cl^- \quad (1)$$

giving a more rapid destruction of pollutants. Anodic oxidation with BDD then seems a suitable procedure to mineralize organics, as found for $HClO_4$ aqueous solutions containing carboxylic acids such as acetic, malic, formic and oxalic [8], 4-chlorophenol [9], phenol [10], and benzoic acid [11], as well as for malic acid at pH 2.7 and ethylendiaminitetraacetic acid at pH 9.2 [12].

The objective of this work is to investigate the electrochemical degradation of methidathion, in aqueous solution using a boron-doped diamond electrode (BDD).

## Materials and methods

Boron-doped diamond films, Diachem®, were synthesized by the hot filament chemical vapor deposition technique (HF CVD) on conducting p-Si substrate (0.1Ω cm, Siltronix).The filament temperature ranged from 2440 to 2560 °C and the substrate one was kept at 830 °C. The reactive gas used was methane in an excess of dihydrogen (1 % $CH_4$ in $H_2$). The doping gas was trimethylboron with a concentration of 3 ppm. The gas mixture was supplied to the reaction chamber, providing a 0.24 $\mu m \cdot h^{-1}$ growth rate for the diamond layer. The diamond films were about 1μm thick. This HF CVD process produces columnar, randomly textured, polycrystalline films.

Electrochemical measurements using a computer controlled by Potentiostat/Galvanostat model PGP 201 associated to "Volta-Master1" software. A conventional three electrodes cell (100 $cm^3$) was used thermoregulated glass cell (Tacussel Standard CEC/TH). Saturated calomel electrode (SCE) and platinum electrode are used as reference and Auxiliary electrodes, respectively. Diamond was used as working electrode (1 $cm^2$ Methidathion [O,O-dimethylS-(5-methoxy-1,3,4-Thiadiazoliny-l-3-methyl) dithiophos-phate] (Fig. 1) is a widely used organophosphorous insecticide, was chosen as the target molecule for the present study because of chemical toxicity (the acute oral $LD_{50}$, for rats is approximately 54 mg/kg [13]).

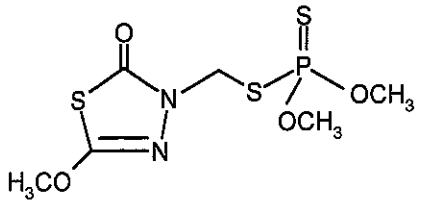


*Fig. 1. Structural formula of methidathion*

Galvanostatic electrolysis ware carried out with a volume of 75 $cm^3$ aqueous solution of methidathion 1.4 $mM \cdot L^{-1}$ during 120 minutes. The range of applied current density was 20 to 60 $mA/cm^2$ and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests have been performed at different temperature in magnetically stirred and aerated solutions. In all cases sodium chloride was added to the electrolytic cell, at different concentrations.

To characterize the toxicity removal, the global parameter, the chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [14]. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5 % margin of experimental error.

The commercial formulation Methidaxide (40 % methidation) was purchased from Bayer. The chemical sodium chloride used was of analytical-reagent grade and was obtained from Aldrich.

## Results and discussions

### *Effect of chloride concentration*

The Fig. 2 shows the effect of chloride ion concentration on the destruction of methidathion, carried out at 60 $mA/cm^2$.

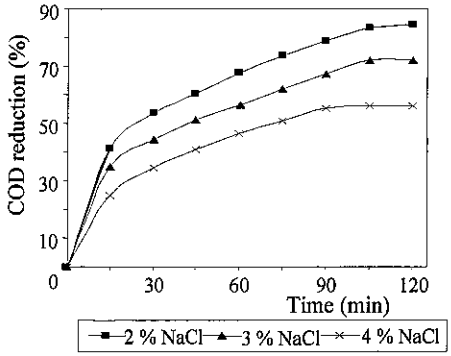


*Fig. 2. The chemical oxygen demand (COD) reduction (in %) for methidathion 1.4 mM/L solution for 120 min of electrolysis at 60 mA and 25 °C*

We observed that the application of electrolysis in this pesticide have the ability to reduce considerably the COD. For example, for 2 % mass NaCl and 3 % NaCl the achieved reduction was 85 % and 72 % respectively, while for 4 % NaCl was 56 %.

The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of methidathion on the electrode or indirect via some mediators like chlorinated species or other radicals [15-16].
Since some oxidant compounds that are produced during oxidation of water (like $O_2$, $O_3$ or hydroxyl radical) or oxidation of chlorine ions following Eq (2) to (4):

$$Cl^- \Leftrightarrow Cl^{\bullet}_{ads} + e^- \quad (2)$$

$$Cl^- + Cl^{\bullet}_{ads} \Leftrightarrow Cl_2 + e^- \quad (3)$$

$$Cl_2 + H_2O \Leftrightarrow HClO + H^+ + Cl^- \quad (4)$$

As cited in reference [17], at pH higher than 4.5 the complete dismutation of $Cl_2$ into HClO and $Cl^-$ is occurred.
An explanation of the mediating role of chloride ions has been proposed by Bonfatti et al [17].
The presence of a weak concentration of chloride ions allows to inhibit the water discharge into oxygen, and to favorise hydroxyl or chloride and oxycloride radicals, which are very powerful oxidants. It can been explain why until 2 % of NaCl concentration the COD removal increases with NaCl concentration.
Increasing the chloride concentration more than 3 % cause a "potentiostatic buffering" by the chlorine redox system and consequently a decrease of the anode potential. Another possibility is the presence of competitive reactions, in particular oxygen and chloride evolution due to recombination of radicals that becomes bigger with the increasing NaCl concentration. The balance of all these phenomena results that there is an optimum of NaCl concentration which is 2 % mass of NaCl for the degradation of methidathion.
Fig. 3 illustrates that the pH during the electrolysis is significantly reduced.

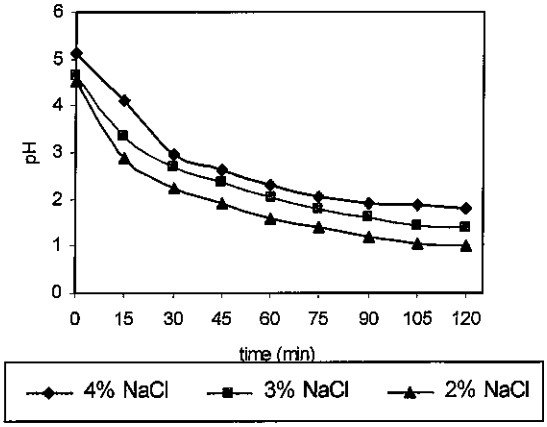


*Fig. 3. PH reduction for methidation 1.4 mM/L solution for 120 min of electrolysis at 60 mA and 25 °C*

Finally the pH in all cases became strong acidic. It is obvious that the continuous addition of high levels of organic matter in the electrolytic cell, resulted in the drop of pH. The electrolysis was more effective in terms of %COD reduction when the pH was in the acid range.
This drop of the pH, during pesticides degradation, was also noted from Kotronarou et al [18]. It was also reported by Bonfatti et al [17] that while the mineralization goes to completion and the solution pH gets more and more acidic.

### *Effect of applied current*

Applied current is an important factor affecting the electrolysis kinetics and process economics. The effect of applied current on the electrochemical process was demonstrated in several studies [19-20]. In Fig. 4 the % COD reduction for the methidathion is presented under different current inputs (chlorides = 2 %).

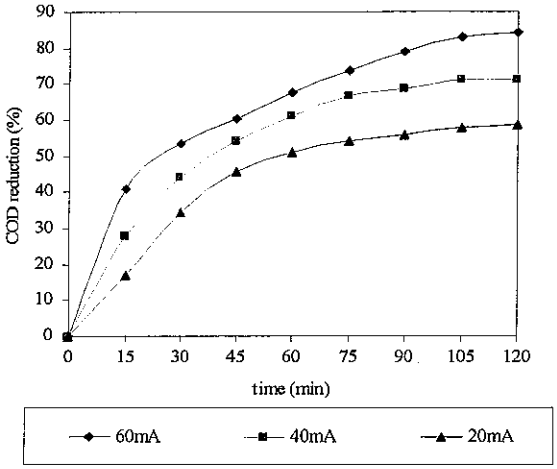


*Fig. 4. COD reduction (in %) for methidathion 1.4 mM/L solution under different current inputs (chlorides = 2 %) and 25 °C*

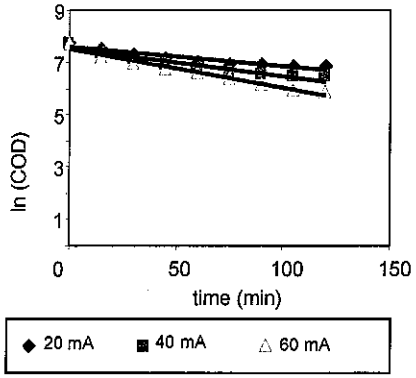


*Fig. 5. Pseudo first-order plot for oxidation of methidathion 1.4 mM/L solution in 2 % NaCl at 25 °C under different current inputs (COD at a given time, t, during electrolysis)*

These studies concluded that applied current increases the rate of electrochemical oxidation process.
The COD of methidathion was observed to fall with pseudo first-order kinetics, on all the surface studied. This is related to the dependence of the rate of oxidation on the rate of formation of the oxidising species at the electrode surface. The pseudo first-order constant of methidathion ($k$) varies from 0.0073 $s^{-1}$ (20 mA) to 0.0146 $s^{-1}$ (60 mA).

This is exemplified in Fig. 5 where the pseudo first-order plot is presented. From these results it was calculated that the best applied current is 60 mA.

### *Effect of temperature*

In Fig. 6 the % COD reduction for methidathion at different temperatures under current input 60 mA is presented.

It is observed that for 25 °C and 65 °C the achieved reduction was 85 % and 66 % respectively.

The COD of methidathion was observed to fall with pseudo first-order kinetics (Fig. 7). The pseudo first-order constant of methidathion ($k$) varies from 0.0131 $s^{-1}$ (25 °C) to 0.0077 $s^{-1}$ (65 °C).

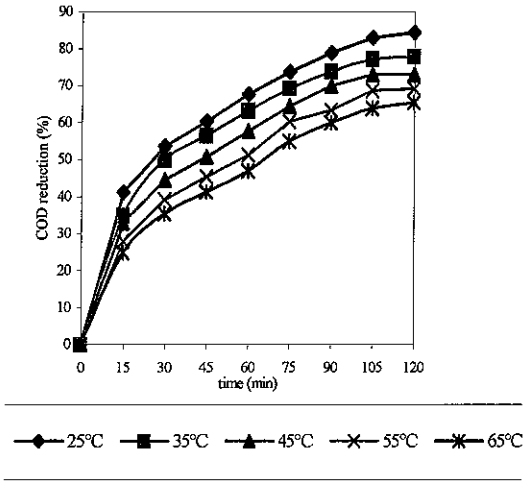


*Fig. 6. COD reduction (in %) for methidathion 1.4 mM/L solution in 2 % NaCl at 25 °C at different temperatures*

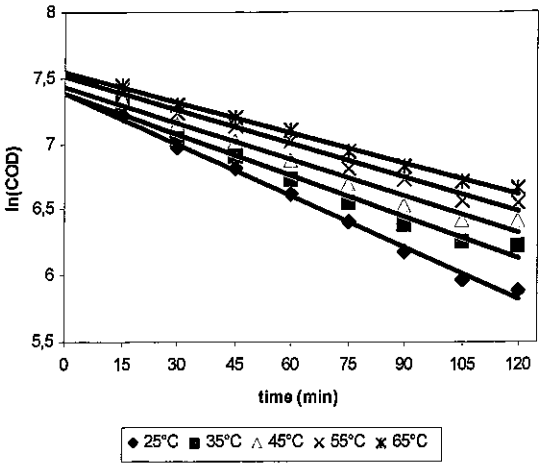


*Fig. 7. Pseudo first-order plot for oxidation of methidathion 1.4 mM/L solution in 2 % NaCl at 60 mA under different temperatures (COD at a given time, t, during electrolysis)*

The effect of temperature on the rates of constant was modelled using the Arrhenius plots, are shown in (Fig. 8). The apparent activation energies were determined by:

$$K = A \cdot \exp(-E_a/RT), \quad (5)$$

where $K$ is rate constant, $A$ is constant, $E_a$ is the activation energy, $T$ is the temperature (K) and $R$ is the gas law constant.

The obtained activation energy (−10.75 kJ) indicates that the process of electrochemical degradation is a complex one.

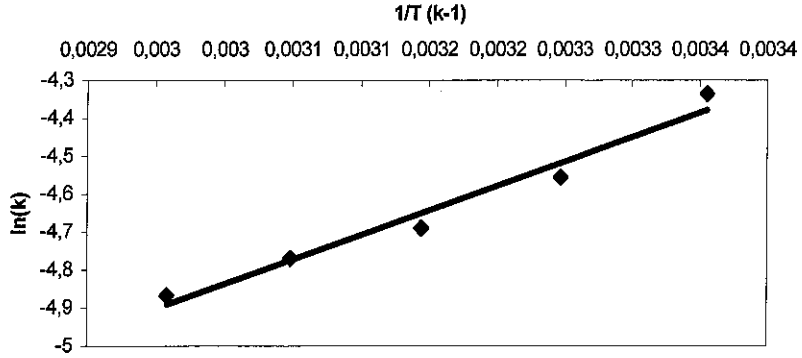


*Fig. 8. Arrhenius plote for oxidation of methidathion 1.4 mM/L solution in 2 % NaCl at 60 mA at various temperatures*

## Conclusions

The conclusions of this study are as follows:

– The application of electrolysis in pesticide has the ability reduce the COD. For 2 % mass NaCl and 3 % mass NaCl the achieved reduction was 85 % and 72 % respectively. For 4 % NaCl was 56 %.

– In all cases the pH of electrolysis was significantly reduced after 45 min.

– The COD of methidathion was observed to fall with pseudo first-order kinetics, on all the surface studied.

– The applied current increases the rate of electrochemical oxidation process.

– The effect of temperature shows that for 25 °C and 65 °C the achieved reduction was 85 % and 66 % respectively.
– The activation energy indicates that the process of electrochemical degradation is a complex one.

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